Study on the formation of phenols during coal flash pyrolysis using pyrolysis-GC/MS

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ABSTRACT

Phenols from coal pyrolysis are extremely precious chemicals, understanding the factors that influence the amounts and species of phenols during coal pyrolysis is of vital importance. In this study, the concentrations of seven species of phenols in the coal extracts were analyzed by GC/MS. Then, the phenols obtained from the pyrolysis of four different coals were characterized by using a flash pyrolysis-GC/MS in-situ. In addition, the amounts of phenols from coal pyrolysis at 400–1000 °C with the heating rate of 10 °C/ms were calculated. Results show that the total amount of phenols during the pyrolysis of lignite (coal A) was higher than those of long-flame coal (coal B), bituminous coal (coal C), and anthracite (coal D) at 800 °C. The main source of phenols is the thermal decomposition of the oxygen-containing structures, particularly aryl ether, rather than the volatilization of the already existing phenols in the raw coal. The formation of phenols, dominated by phenol and cresols, is facilitated during the coal pyrolysis at 600–800 °C, otherwise, certain phenols may be decomposed at higher temperatures. Moreover, there is close correlation between the release amount of phenols and the specific surface area of the coal during coal pyrolysis.

1. Introduction

As an important intermediate stage in coal conversion, pyrolysis is also considered to be a simple and effective method for the clean conversion of coal [1]. For example, low temperature carbonization is often used for phenols products [2]. Tremendous efforts have been devoted to study coal pyrolysis and its product distribution [3–7], including the characterization of composition and mass distribution of coal-derived liquids [8–10], in which high value-added chemicals, especially phenolic compounds, have been separated. However, most of the studies on characterizing products of coal pyrolysis have been performed indirectly by collecting coal tar [1,3,4,9]. Meanwhile, some in-situ studies have been reported [10–14]. With the pyrolysis-GC/MS (pyrolysis-gas chromatography–mass spectrometry) used, Dong et al. [12,13] investigated the principle and formation mechanism of PAHs (polycyclic aromatic hydrocarbons), and Fabiańska et al. [14] investigated the polar compounds in lignite. Considering the adverse effect of the condensation of pyrolysis vapors on the analyses of phenols, it is important to propose a method for investigating the formation of phenols, especially alkyl phenols, in detail during coal pyrolysis on-line.

The flash pyro-probe is a powerful tool to carry out rapid pyrolysis without secondary reactions, in which both high heating rates and better contact of the coal particles may be achieved. As a useful tool in the study of the composition of the volatile fraction during coal pyrolysis [15], GC/MS can provide a better method for the quantitative and qualitative analyses of complex mixtures with high efficiency, precision, and simplicity [16,17]. Therefore, the flash pyrolysis-GC/MS that has been used in the structure study of coals can provide information in-situ at molecular level, particularly in the presence of phenolic forms [18–20]. More importantly, the direct information about the amounts and species of phenols released during coal pyrolysis can be obtained, and the effect of the condensation of pyrolysis vapors on the analyses of phenolic compounds can be avoided.

To ascertain the source of phenolic compounds during coal pyrolysis, dichloromethane (CH_2Cl_2) was applied to extract the phenolic compounds in the raw coal, the formation and distribution characteristics of phenols generated during the raw coal and residue pyrolysis were also analyzed by flash pyrolysis-GC/MS on-line. By comparing these two parts, the actual source of phenols can be established. A multi-step program, that could be used to perform the pyrolysis experiment of the same coal sample at different temperatures, was applied in this study to gain a more fundamental understanding of the phenols during coal pyrolysis, including the amounts and species of phenolic compounds with temperatures. In addition, the effects of the coal rank on the formation and

distribution characteristics of phenolic compounds during coal pyrolysis were also investigated.

Thus, this study was aimed to provide the formation and distribution characteristics of phenols generated during different coal pyrolysis at different temperatures by flash pyrolysis-GC/MS analysis on-line. Moreover, the effect of CH_2Cl_2 extraction on the phenols formation during coal residue pyrolysis and the formation mechanism of phenols during coal pyrolysis were also discussed by qualitative and quantitative analyses with flash pyrolysis-GC/MS.

2. Experimental

2.1. Coal samples and chemicals

Four coal samples including lignite (coal A), long-flame coal (coal B), bituminous coal (coal C), and anthracite (coal D) from China were used in the study. The raw coals were ground to 0.15–0.30 mm and used as the experimental samples. The proximate and ultimate analyses of the coal samples were performed by chemical analysis methods according to GB/T 212-2008 (for moisture, ash, and volatile), GB/T 476-2008 (for C, H), GB/T 19227-2008 (for N) and GB/T 214-2007 (for S), and the analytical values are listed in Table 1.

Seven species of common phenolic compounds were analyzed, such as phenol, o-cresol, m-cresol (p-cresol), 2,4-xylenol (2,5-xylenol), 2,6-xylenol, 3,4-xylenol, and β-naphthol. Each standard was obtained from Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China.

2.2. Solvent extraction

Each of the raw coal samples (2.00 g) was extracted with 120 mL CH_2Cl_2 in an automated extraction system (Gerhardt Soxtherm macro 414) at 120 °C for about 6 h. The extract yield (wt%) is expressed as follows:

$$wt\% = \frac{100 \times (m_1 - m_2)}{m \times (100 - M_{ad} - A_{ad})} \times 100\%$$

where m is the weight of the coal sample, m_1 and m_2 are the total weight of the coal sample and filter before and after extraction, respectively. After concentrating the extracted solution to 1 mL using a pressure blowing concentrator, 1 μL of the solution was injected into the GC/MS in the splitless mode.

2.3. Pyrolysis-GC/MS analysis

With two pieces of quartz wool placed at the top and bottom, 1.00 mg coal sample, supported by the quartz rod, was applied in a quartz tube for each pyrolysis experiment. Each of the sample was pyrolyzed using a pyro-probe (CDS-5250, CDS Analytical Inc.) equipped with a multi-step temperature controller, and then phenols obtained were analyzed on-line by GC/MS (Focus GC-DSQII, Thermo Fisher Scientific), running automatically for each
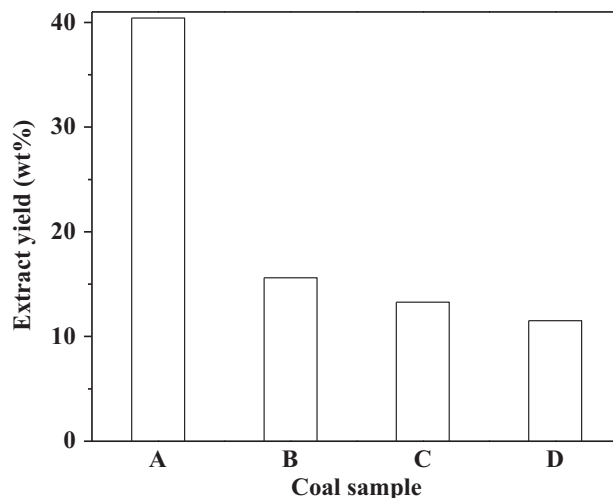

Fig. 1. Extract yield of different coal samples.

temperature step. The multi-step temperature programming included up to eight GC runs per sample; the final temperatures, 400, 500, 600, 700, 800, 900, and 1000 °C were reached at a heating rate of 10 °C/ms for each coal sample. In fact, the heating rate was much lower than 10 °C/ms [21]. In contrast, the actual temperature was higher than the nominal at low temperatures, and this difference become negligible for temperatures higher than 1000 °C [22].

The pyrolyzed non-condensable volatiles, without trapped, were transferred in the GC injection port through the transfer line heated at 275 °C and then separated using a TG-5MS (Thermo Fisher Scientific) capillary column (30 m × 0.25 mm × 0.25 μm). The initial oven temperature was 50 °C and held for 2 min, subsequently, it was programmed from 50 to 100 °C at a rate of 10 °C/min without an isothermal held, and then increased to 150 °C at a rate of 3 °C/min and held constant for 2 min. Finally, the oven temperature was increased to 300 °C at a rate of 8 °C/min with an isothermal held for 5 min. Helium (99.999%) was employed, as the carrier gas, at a constant flow rate of 1.0 mL/min. The injection port and transfer line temperatures were maintained at 310 °C and 250 °C, respectively. The analyses were performed in the SIM (selected ion monitoring) mode in order to achieve greater selectivity and sensitivity for phenols when entering the mass spectrometer.

2.4. Phenols analysis method

The standard compounds of phenols were directly injected into the GC/MS in the splitless mode. The GC analysis was 5-min solvent delayed to avoid the large solvent peak signal. By comparing the retention times of samples and standard compounds and their mass spectral data with MS libraries, phenolic compounds were identified and detected. A series

Table 1
Proximate and ultimate analyses (wt.%) of the coal samples.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t, ad}$
	M_{ad}	A_{ad}	V_{daf}	C	H	O[b]	N	
Coal A[a]	29.80	6.21	45.94	74.87	3.45	>17.51	1.20	1.90
Coal B	12.61	5.43	33.80	71.97	4.01	>22.41	1.17	0.36
Coal C	2.23	17.93	37.19	80.41	5.20	>11.95	1.38	0.85
Coal D	0.74	15.45	7.49	89.81	3.21	>5.61	1.07	0.26

ad: air dried basis; daf: dry and ash-free basis; $S_{t, ad}$: total sulfur (air dried basis).

[a] Coals A, B, C and D were brought from Inner Mongolia, Shanxi, Xinjiang, and Shanxi province of China, respectively.

[b] By difference.

Table 2
Amounts of phenols in the coal extracts (μg/g)[a].

Sample	Phenol	o-Cresol	m-Cresol[c]	2,4-Xylenol[c]	3,4-Xylenol	2,6-Xylenol	β-Naphthol	Phenols
EA[b]	0.02	0.06	0.20	0.04	0.06	0.01	0.33	0.72
EB[b]	0.03	0.01	0.04	0.01	0.03	0.02	0.19	0.34
EC[b]	0.17	0.13	0.19	0.23	0.60	0.13	0.94	2.40
ED[b]	0.01	0.01	0.03	0.01	0.02	0.01	0.04	0.11

[a] The range of standard deviation for data in the table is ± 0.00–0.14.
[b] EA, EB, EC and ED refer to CH_2Cl_2 extracts of Coal A, B, C and D, respectively.
[c] m-Cresol refer to m-cresol and p-cresol, 2,4-xylenol refer to 2,4-xylenol and 2,5-xylenol, they are inseparable under the experimental conditions.

of spike solutions at 0.1–1.0 μg/mL concentrations of all the standards were prepared from the stock solutions (0.1 mg/mL) by diluting with CH_2Cl_2, as the solvent. Each of the phenols concentration was calculated using an external standard line in the GC/MS.

3. Results and discussion

3.1. Phenols in the raw coal

The extract yields of different coal samples and the contents of the seven species of phenolic compounds in the four coals are shown in Fig. 1 and Table 2, respectively. Fig. 1 suggested that the extract yield of the coal sample decreased with the coal rank.

A comparison between Fig. 1 and Table 2 shows no direct relevance between the concentration of phenols in the extracts and the extract yields of the coal samples. The difference in phenols among the four extracts may be not only attributed to the contents of oxygen, but also to the forms of oxygen-containing compounds in coals. Phenolic hydroxyl is the main O-containing functional group in bituminous coal [23]; however, carboxylic acid, ester, and ether are the main O-containing groups in lignite (also in long-flame coal) [24]. Further, ether and oxygen heterocyclic are the main O-containing groups in anthracite [25]. Therefore, it may be inferred that higher phenolic hydroxyl in bituminous coal has strong relativity with the concentration of phenols in coal extract, since the amount of phenols in coal C is the highest among the four coals.

Table 2 lists the concentrations of the seven species of phenols in the coal extracts by external standard method. The most abundant phenolic species in coal extraction is β-naphthol, irrespective of the coal rank, indicating that bicyclic organic matter is the main substance in the coal extracts of different coal samples.

3.2. Release of phenols during coal pyrolysis

Phenols are mainly formed in the temperature range of 600–800 °C, as discussed in Section 3.3. Therefore, the amount of phenolic compounds released during coal pyrolysis at 800 °C was determined, as shown in Table 3. Unlike the data of the coal extracts, the amounts of phenols released during coal A, B, and C pyrolysis at 800 °C were 2317, 1015, and 1100 μg/g, respectively, much higher than that of coal D (1.16 μg/g). Large amounts of phenolic compounds formed during coal A, B, and C pyrolysis, to a great degree, are associated with their higher oxygen content and O-containing structures, particularly aryl ether, which can be pyrolyzed to form phenols. Further, the minimal oxygen content was found in coal D, i.e., phenolic compounds were scarcely detected.

Table 3 shows the largest amount of phenol and cresols, as the phenolic products, during the raw coal pyrolysis, i.e., 56.8%, 46.5%, and 87.9% of phenol for coal A, B, D, respectively, and 41.5% of cresols for coal C. In all the extracts of the raw coals, largest amounts of β-naphthol were observed, indicating that a part of aryl ethers attached to phenyl or alkylbenzene can be decomposed to form phenol and cresols during coal pyrolysis.

Tables 2 and 3 show that the amount of phenols obtained from the coal pyrolysis was much higher than that in the coal extracts. Under the heating conditions, the weak C–C and C–O bonds of diverse types of linkages, such as ether linkages, connecting condensed aromatic and hydroaromatic units in the coal macromolecular structure were cleaved [26–29]. Thus, the emission of phenolic compounds during the coal pyrolysis is largely due to the thermal cracking of oxygen-containing structures rather than the escape of phenols already existing in the raw coals.

3.3. Effect of pyrolysis temperature on the release of phenolic compounds

Each coal sample was sequentially pyrolyzed at 400, 500, 600, 700, 800, 900, and 1000 °C, and the seven species of phenolic compounds were on-line analyzed by the GC/MS. The amounts of phenolic compounds in the pyrolysis products of the raw coals at different temperatures are listed in Table 4.

Least amounts of phenols were generated from the raw coal pyrolysis at 400 or 1000 °C. With the increase in temperature, the total phenolic compounds generated at the different temperature stages increased gradually; however, it reached the maximum value at 700 °C. Incidentally, the relative increases in phenol and cresols were significant. Phenol generated during coal A and D pyrolysis reached the peak value at 700 °C; however, the maximum phenol generation temperature of coals B and C increased further to 800 °C. In addition, all the seven species of phenolic compounds were produced during coal pyrolysis with temperatures reaching 600 °C and 700 °C, indicating that this temperature range is favorable for the formation of the phenolic compounds [27], and the decomposition reaction of phenolic compounds may occur at higher temperature.

Table 3
Amounts of phenols in the products of raw coal pyrolysis at 800 °C (μg/g)[a].

Sample	Phenol	o-Cresol	m-Cresol[b]	2,4-Xylenol[b]	3,4-Xylenol	2,6-Xylenol	β-Naphthol	Phenols
Coal A	1317	191.5	619.6	63.62	24.32	50.45	50.24	2317
Coal B	471.8	110.2	303.2	50.00	11.24	29.79	38.68	1015
Coal C	441.9	145.2	311.7	85.80	63.55	38.30	13.34	1100
Coal D	1.02	0.04	0.07	–[c]	–	0.03	–	1.16

[a] The range of standard deviation for data in the table is ± 0.00–132.
[b] m-Cresol refer to m-cresol and p-cresol, 2,4-xylenol refer to 2,4-xylenol and 2,5-xylenol, they are inseparable under the experimental conditions.
[c] Not detected.

Table 4
Contents of phenolic compounds from the raw coal pyrolysis at different temperatures (μg/g, n = 4)[a].

| Phenols	Sample	T/°C						
		400	500	600	700	800	900	1000
Phenol	Coal A	–[b]	1.81	297.1	748.4	269.8	1.62	–
	Coal B	0.01	0.45	54.91	143.6	272.8	1.80	0.12
	Coal C	–	–	61.86	174.5	205.5	1.32	–
	Coal D	–	–	0.37	0.38	0.27	–	–
o-Cresol	Coal A	0.01	0.04	23.34	148.9	19.21	–	–
	Coal B	–	0.01	4.48	54.42	51.33	0.06	–
	Coal C	–	–	13.68	98.39	33.10	–	–
	Coal D	–	–	0.02	0.01	0.01	–	–
m-Cresol[c]	Coal A	0.02	0.18	100.2	464.1	55.15	0.03	–
	Coal B	–	0.05	19.92	163.8	119.5	0.19	–
	Coal C	–	–	32.98	209.5	69.31	0.06	–
	Coal D	–	0.01	0.02	0.02	0.02	–	–
2,4-Xylenol[c]	Coal A	–	–	6.56	57.06	–	–	–
	Coal B	–	–	0.29	28.11	21.60	–	–
	Coal C	–	–	2.52	72.71	10.57	–	–
	Coal D	–	–	–	–	–	–	–
2,6-Xylenol	Coal A	–	–	6.65	14.62	3.05	0.02	–
	Coal B	–	–	2.37	5.88	2.98	0.02	–
	Coal C	–	–	10.54	37.38	15.63	0.02	–
	Coal D	–	–	–	–	–	–	–
3,4-Xylenol	Coal A	0.01	0.02	8.46	24.33	17.63	0.03	–
	Coal B	–	–	0.85	22.64	6.29	–	–
	Coal C	–	–	6.70	22.02	9.58	–	–
	Coal D	–	–	0.01	0.01	0.01	–	–
β-Naphthol	Coal A	–	0.01	3.24	37.71	9.28	–	–
	Coal B	–	–	–	18.11	20.56	–	–
	Coal C	–	–	2.06	11.28	–	–	–
	Coal D	–	–	–	–	–	–	–
Phenolic compound	Coal A	0.03	2.06	445.5	1495	374.1	1.70	–
	Coal B	0.01	0.51	82.83	436.6	495.0	2.07	0.12
	Coal C	–	0.01	130.3	625.8	343.7	1.40	–
	Coal D	–	0.01	0.41	0.41	0.30	–	–

[a] The range of standard deviation for data in the table is ± 0.00–85.
[b] Not detected.
[c] m-Cresol refer to m-cresol and p-cresol, 2,4-xylenol refer to 2,4-xylenol and 2,5-xylenol, they are inseparable under the experimental conditions.

The trend of the generation of other species of phenolic compounds with the variation of temperature was similar to that of the phenol: first increases and then decreases. During the pyrolysis of coal D, three species of xylenols and β-naphthol were generally below the test limit; a slight generation of phenolic compounds was observed during the pyrolysis of the other three coals at 400, 500, 900, and 1000 °C. In certain cases, it was even undetectable. However, in the other temperature stages, certain amounts of the seven species of phenols were generated during the pyrolysis of coal A, B, and C, indicating that enough energy was provided for the thermal cracking of the oxygen-containing functional groups to afford the phenolic compounds during the coal pyrolysis at 600 to 800 °C. After that temperature range, few oxygen-containing groups were left to decompose at the higher temperature range of 900 to 1000 °C, even though significantly more energy was provided. In addition, the increase in the total phenolic compounds was mainly the contribution of phenol and cresols.

By comparing the amount of phenols generated from the low-temperature cracking of the raw coal at 400 °C to that existing in the raw coal, the total phenolic compounds generated by the former were 0.03, 0.01, 0 and 0 μg/g for coals A, B, C, and D, respectively, which were definitely less than that (0.72, 0.34, 2.40, and 0.11 μg/g) in the latter. Therefore, the release of extractable phenolic compounds from the raw coal was not merely because of the evaporation; they probably underwent other reactions for the transformation during the coal pyrolysis at 400 °C. Thus, further investigations were needed for the pyrolysis at even lower temperatures.

As outlined above, phenols are mainly generated by the thermal cracking of O-containing macromoleculars in coal. The amounts and species of phenolic compounds generated under the same coal pyrolysis conditions depend to some extent on the properties of coal. Coals B and

C are bituminite with a higher degree of condensation of aromatic ring than coal A, therefore, the amount of phenols from coal A pyrolysis was found to be higher than those from coal B and C pyrolysis below 700 °C. In contrast, more phenolic compounds were obtained during the pyrolysis of coals B and C above 700 °C.
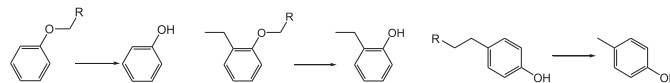
During the coal flash pyrolysis, phenolic compounds separated from
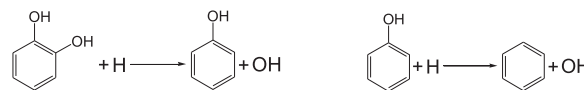
the gaseous products are generated by the cleavage of ether bond of aryl ethers in the temperature range of 500–800 °C, similar to that in a polymer in which the aryl ether segments are bonded through keto and methylene groups to the neighboring segments [26–28].

Above 700 °C, the decomposition reactions of the phenolic compounds in the coal may be intensified [30].

3.4. Principle of phenols formation during the pyrolysis of coal residues

To prove that the phenols were mainly generated by pyrolysis reactions, four coal residues, in which some small molecular compounds

Table 5
Amounts of phenols generated during the coal residues pyrolysis at 800 °C (µg/g)[a].

Sample	Phenol	o-Cresol	m-Cresol[d]	2,4-Xylenol[d]	3,4-Xylenol	2,6-Xylenol	β-Naphthol	Phenols
AR[b]	1542	301.3	816.2	125.5	60.12	35.11	97.10	2978
BR[b]	579.8	106.8	353.2	43.71	16.64	33.04	53.32	1187
CR[b]	541.8	270.3	550.1	162.0	80.69	81.39	64.62	1751
DR[b]	1.03	–[c]	–	–	–	0.01	–	1.04

[a] The range of standard deviation for data in the table is ± 0.00–169.
[b] AR, BR, CR and DR refer to the coal residues after the CH_2Cl_2 extraction of coals A, B, C and D, respectively.
[c] Not detected.
[d] m-Cresol refer to m-cresol and p-cresol, 2,4-xylenol refer to 2,4-xylenol and 2,5-xylenol, they are inseparable under the experimental conditions.

had been extracted out with CH_2Cl_2, were pyrolyzed in the study. The amounts of phenols obtained from the pyrolysis of the residues of coals A, B, C and D are shown in Table 5. The total amounts of phenols obtained were more than that during the raw coal pyrolysis except for coal D and DR (residue of coal D).

Tables 2, 3 and 5 show that the total amounts of phenolic compounds in coal extracts were much poorer, which were richer during the corresponding residue pyrolysis than that from the raw coal pyrolysis. And phenol and cresols obtained during both residues and raw coal pyrolysis accounted for majority in seven species of phenolic compounds. This is a powerful evidence for the hypothesis that the phenolic compounds generated during the coal pyrolysis were originated in the cleavage of the oxygen-containing structure in coal, and the already existing phenolic compounds in the raw coal play a minor role.

The pore structure of coal not only reflects the specific surface area but also significantly affects its thermal behavior [31]. The coal macromolecular network structure was infiltrated and swelled by the solvent molecules during the solvent extraction, and most of the micromolecular compounds in coal were extracted, thus resulting in the enlarging in the pore size [32] and the increase in the specific surface area of the coal, as showed in Table 6.

During the raw coal pyrolysis, the deposition of coal tar vapors may occur on the surfaces of pyrolyzed coal, and partially of tar vapors re-polymerize to form coal char or crack to generate lighter products [33]. On the other hand, the well-developed pore structure of the coal residues promoted precipitation of volatiles and diffusion of gaseous reactants. Consequently, the emission of phenols from the pyrolysis of coal residues was higher than that from the raw coal, probably due to the change in the coal structures during the CH_2Cl_2 extraction process. Obviously, the formation of phenols was enhanced by this pretreatment during the pyrolysis of the coal residues.

4. Conclusions

(1) The total amount of phenols generated from the pyrolysis (800 °C) of lignite (coal A, 2317 µg/g) was significantly higher than those of long-flame coal (coal B, 1015 µg/g), bituminite (coal C, 1100 µg/g), and anthracite (coal D, 1.16 µg/g). Further, phenols generated from the pyrolysis of different ranks of coals and residues were dominated by phenol and cresols.

(2) The phenolic compounds were mainly generated by the thermal decomposition of the O-containing structures rather than the volatilization of the already existing phenols in the raw coal during the flash pyrolysis. The release of phenols during the flash pyrolysis may be promoted by changing the specific surface area of the coal during the CH_2Cl_2 extraction.

(3) The amounts and species of phenols obtained during the flash

pyrolysis of coals and coal residues were the highest in the temperature range of 600–800 °C, probably due to the enhancement in the thermal cracking of the oxygen-containing structures, particularly the aryl ether.

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Table 6
Brunauer-Emmett-Teller specific surface areas of the coal samples (m²/g).

Sample	Coal A	Coal B	Coal C	Coal D
Raw coal	2.237	2.246	2.065	1.602
Coal residue	2.494	2.674	2.401	2.182

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